

IN THE UNITED STATES PATENT AND TRADE MARK OFFICE

In re Patent Application of  
Yuka, OTOMARU et al.

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For: TRANSITION METAL COMPLEXES AND POLYMERIZATION CATALYSTS

DECLARATION OF Hidenori HANAOKA UNDER 37 C.F.R. 1.132

Sir:

I, Hidenori HANAOKA, a citizen of Japan, residing at 5-3-8-306 Furuedai, Suita-shi, Osaka, Japan declare that:

I majored in organic chemistry and completed the master's course of OSAKA University, Faculty of Engeneering Science in March, 1993.

I joined Research Laboratories at Osaka of Sumitomo Chemical Company, Limited and have been engaged in the research of polymerization catalyst since August, 1994.

I am the inventor of the above-identified application and am familiar with the subject matter thereof.

I have read the Office Action mailed with references cited therein.

Following experiments were made under my directions in order to show that the presently claimed invention has an unexpected superior results over W087/02370 to Kakugo et al.

## Experiments

### 1) Examples 1 to 7

Examples 1 to 7 were conducted by using a chromium complex of the invention having 2,2'-phenylphosphidobis(6-tert-butyl-4-methylphenol) as a ligand.

#### Example 1

5.0 mL of toluene was placed into a 23.5 mL autoclave under nitrogen, and stabilized at 40°C., and then ethylene was pressurized to 0.60 MPa therein and stabilized. Methylaluminoxane (100  $\mu\text{mol}$ ), and 2,2'-(phenylphosphido)bis(6-tert-butyl-4-methylphenoxy)chromium chloride (0.10  $\mu\text{mol}$ ) were added thereto to perform polymerization for 30 minutes. As a result of polymerization,  $1.08 \times 10^7$  g of a polymer was prepared per 1 mol of chromium an hour.

#### Example 2

According to the same manner as that of Example 1 above except that a solution of triisobutylaluminum in hexane (40  $\mu\text{L}$ , 1.0 M, Kanto Kagaku) and pentafluorophenylborane (0.30  $\mu\text{mol}$ ) were used in place of methylaluminoxane, polymerization was performed. As a result of polymerization,  $4.00 \times 10^6$  g of a polymer was prepared per 1 mol of chromium an hour.

Examples 3 to 7 were conducted in a similar manner as in Example 1 except using each catalyst component or components noted in the Table 1 below.

### 2) Comparative Examples 1 to 9

Comparative Examples 1 and 2 were conducted by using titanium complex containing 2,2'-(phenylphosphido)bis(6-tert-butyl-4-methylphenol) as the ligand and Comparative Examples 3 to 6 were conducted by using

2,2'-thiobis(6-tert-butyl-4-methylphenol) as ligand disclosed by Kakugo et al.

Comparative Examples 7 to 9 were conducted by using chromium complex containing 2,2'-thiobis(6-tert-butyl-4-methylphenol) as a ligand.

#### Comparative Example 1

5.0 mL of toluene was placed into a 23.5 mL autoclave under nitrogen, and stabilized at 40°C, and then ethylene was pressurized to 0.60 MPa therein and stabilized. A solution of triisobutylaluminum in hexane (40  $\mu$ L, 1.0 M, Kanto Kagaku), triphenylmethyl tetrakis(pentafluorophenyl)borate (0.30  $\mu$ mol) and 2,2'-(phenylphosphido)bis(6-tert-butyl-4-methylphenoxy)(tetrahydrofuran)titanium dichloride (0.10  $\mu$ mol) were added thereto, and polymerization was carried out for 30 minutes. As a result of polymerization,  $1.30 \times 10^6$  g of a polymer was prepared per 1 mol of titanium an hour.

#### Comparative Example 2

5.0 mL of toluene and 1-hexene (50  $\mu$ L) were placed into a 23.5 mL autoclave under nitrogen, and stabilized at 40°C, and then ethylene was pressurized to 0.60MPa therein and stabilized. A solution of triisobutylaluminum in hexane (40  $\mu$ L, 1.0 M, Kanto Kagaku), dimethylanilinium tetrakis(pentafluorophenyl)borate (0.30  $\mu$ mol) and 2,2'-(phenylphosphido)bis(6-tert-butyl-4-methylphenoxy)(tetrahydro-furan)titanium dichloride (0.10  $\mu$ mol) were added thereto, and polymerization was carried out for 30 minutes. As a result of polymerization,  $7.00 \times 10^5$  g of a polymer was prepared per 1 mol of titanium an hour.

#### Comparative Example 3

5.0 mL of toluene were placed into a 23.5 mL autoclave under nitrogen, and stabilized at 40°C, and then ethylene was pressurized to 0.60MPa therein and stabilized. Methyaluninoxane(100  $\mu$ mol) and

2,2'-thiobis(6-tert-butyl-4-methylphenoxy)titanium dichloride (0.10  $\mu\text{mol}$ ) were added thereto, and polymerization was carried out for 30 minutes. As a result of polymerization,  $8.5 \times 10^6$  g of a polymer was prepared per 1 mol of titanium an hour.

#### Comparative Examples 4 to 6

Comparative Examples 3 to 6 were conducted in a similar manner as in Comparative Example 1 except using each catalyst component or components as listed in the following Table 2 below.

#### Comparative Examples 7

5.0 mL of toluene were placed into a 23.5 mL autoclave under nitrogen, and stabilized at 40°C, and then ethylene was pressurized to 0.60MPa therein and stabilized. A solution of triisobutylaluminum in hexane (40  $\mu\text{L}$ , 1.0 M, Kanto Kagaku), pentafluorophenylborane (0.30  $\mu\text{mol}$ ) and a chromium complex in toluene solution obtained by contacting 2,2'-thiobis(6-tert-butyl-4-methylphenoxy)titanium dichloride (0.20  $\mu\text{mol}$ ) with  $\text{CrCl}_3(\text{tetrahydrofuran})_3$  (0.20  $\mu\text{mol}$ ) at 25°C for 1 minutes, were added thereto, and polymerization was carried out for 30 minutes. As a result of polymerization,  $1.9 \times 10^6$  g of a polymer was prepared per 1 mol of titanium an hour.

#### Comparative Examples 8 and 9

Comparative Examples 8 and 9 were conducted in a similar manner as in Comparative Example 7 except using each catalyst component or components as listed in the following Table 2 below.

#### 2) Results and conclusions:

2,2'-(phenylphosphido)bis(6-tert-butyl-4-methylphenoxy)(tetrahydrofuran)titanium dichloride showed lower polymerization activity as shown in Comparative Examples 1 and 2. Mere change of ligands within the broad disclosure of Kakugo et al does not produce catalyst of higher activity.

The catalysts of the present invention comprising chromium

complex show higher polymerization activity, which can be confirmed their use with any catalyst component. (see Example 1 vs. Comparative Example 3, Example 2 vs. Comparative Example 4, Example 3 vs. Comparative Example 5, Example 4 vs. Comparative Example 6)

Polymerization activities of the catalyst of the present invention comprising chromium complex of ligand I show higher activity than the chromium complex of ligand II(see Examples 5 to 7 vs. Comparative Examples 7 and 8).

Thus, one skilled in the art cannot arrive at the present invention characterized by a specific metal and a characteristic ligand from the mere broad generic disclosure. The higher polymerization catalyst activity of the present invention is unexpected in view of the disclosure of Kakugo et al.

The undersigned declares further that all statements made herein of his knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fined or imprisonment, or both under 18 U.S.Code 1001 and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

This *2<sup>nd</sup>* day of March 2007

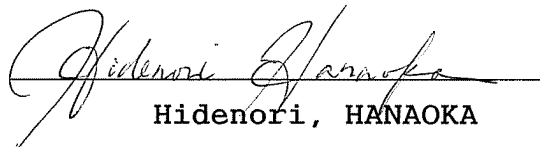
  
Hidenori, HANAOKA

Table 1 Ethylene Polymerization Reaction Results

Example	1	2	3	4	5	6	7
Metal	Cr	Cr	Cr	Cr	Cr	Cr	Cr
Ligand	I	I	I	I	I	I	I
Component 1	A1	A2	A2	A2	A2	A2	A2
Component 2	-	A3	A4	A5	A3	A4	A5
Polymer g/Cr/hr	1.08 $\times 10^7$	4.00 $\times 10^6$	1.70 $\times 10^7$	7.72 $\times 10^7$	8.10 $\times 10^6$	1.29 $\times 10^7$	4.87 $\times 10^7$

Ligand I: 2,2'-(phenylphosphido)bis(6-tert-butyl-4-methylphenol)

Component A1: Methylaluminoxane

Component A2: Triisobutylaluminum in hexane (40  $\mu$ L, 1.0 M)

Component A3: Pentafluorophenylborane (0.30  $\mu$ mol)

Component A4: Dimethylanilinium tetrakis(pentafluorophenyl)borate (0.30  $\mu$ mol)

Component A5: Triphenylmethyl tetrakis(pentafluorophenyl)borate (0.30  $\mu$ mol)

Table 2 Ethylene Polymerization Reaction Results of Comparative Examples

Comparative Example	1	2	3	4	5	6	7	8	9
Metal	Ti	Ti	Ti	Ti	Ti	Ti	Cr	Cr	Cr
Ligand	I	I	II	II	II	II	II	II	II
Component 1	A2	A2	A1	A2	A2	A2	A2	A2	A2
Component 2	A3	A4	-	A3	A4	A5	A3	A4	A5
Polymer g/Cr/hr	1.3 x 10 <sup>6</sup>	7.00 x 10 <sup>5</sup>	8.5 x 10 <sup>6</sup>	0.6 x 10 <sup>6</sup>	6.2 x 10 <sup>6</sup>	5.9 x 10 <sup>6</sup>	1.9 x 10 <sup>6</sup>	0.5 x 10 <sup>6</sup>	0.6 x 10 <sup>6</sup>

Ligand I: 2,2'-(phenylphosphido)bis(6-tert-butyl-4-methylphenol)

Ligand II: 2,2'-thiobis(6-tert-butyl-4-methylphenol)

Component A1: Methylaluminoxane

Component A2: Triisobutylaluminum in hexane (40  $\mu$ L, 1.0 M)

Component A3: Pentafluorophenylborane (0.30  $\mu$ mol)

Component A4: Dimethylanilinium tetrakis(pentafluorophenyl)borate (0.30  $\mu$ mol)

Component A5: Triphenylmethyl tetrakis(pentafluorophenyl)borate (0.30  $\mu$ mol)